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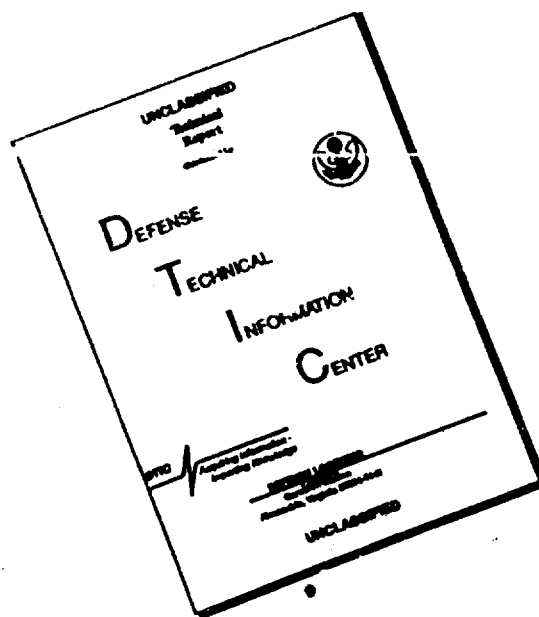


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Quenching Rate Constants of $\text{NF}(a^1\Delta)$ by N_2F_4 , NF_3 , NF_2 , $\text{NF}(\text{X})$, SiF_4 , HNCO , and NCO at Room Temperature

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A flow reactor has been used to measure the room temperature rate constants for quenching of $\text{NF}(a^1\Delta)$ by molecules containing the NF bond and by SiF_4 , HNCO , and NCO . The quenching rate constants decrease in the series $\text{NF}(\text{X})$, N_2F_4 , NF_2 , and NF_3 . The rate constant for $\text{NF}(\text{X})$ is $(3 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is smaller than the bimolecular self-destruction rate constant of $\text{NF}(a)$. The quenching rate was so slow for NF_3 that only an upper limit to the rate constant, $1.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, could be measured. The quenching constant for SiF_4 is also small, $\sim 1.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constants for HNCO and NCO were measured because these molecules were utilized in the generation of $\text{NF}(\text{X})$; estimates for their rate constants are $(4.5 \pm 1.0) \times 10^{-13}$ and $(7.0 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quenching constants for HNCO and NCO are consistent with those for other carbonyl-containing molecules.

Introduction

The rate constants for quenching of $\text{NF}(a^1\Delta)$ by a series of stable molecules and a few reactive atoms have been reported previously from this laboratory using the flow reactor technique.¹⁻⁵ The $2\text{F} + \text{HN}_3$ reaction was used as the source of the metastable $\text{NF}(a)$ molecule, which has a radiative lifetime of 5–6 s.⁶ The mechanisms for quenching of $\text{NF}(a)$ by stable molecules can be divided into two broad categories: those proceeding by chemical reaction and those resulting in physical deactivation to $\text{NF}(\text{X}^2\Sigma^-)$. The magnitude of the rate constants for molecules in the first category correlates with the basicity of the reagents that could act as Lewis bases and with the ionization energy of the unsaturated molecules. Many of the chemical reactions probably involve addition and insertion mechanisms, giving adducts that correspond to ground states. One example is the $\text{NF}(a) + \text{CO}$ reaction; the primary step is formation of chemically activated FNCO , which subsequently dissociates to $\text{F} + \text{NCO}$.⁷ The chemical reactions of atoms and small molecules with $\text{NF}(a)$ that have small rate constants presumably have potential energy barriers in the entrance channel. The only reactions of $\text{NF}(a)$ for which physical quenching has been proven by product analysis are with I , I_2 , IF , and ICl , but quenching by N_2 , HF , and many perfluorinated molecules is energetically constrained to give $\text{NF}(\text{X})$. Physical quenching by electronic-to-vibrational energy transfer has very slow rates, unless there are attractive interaction potentials. The quenching constants for open-shell atoms, which normally are considered to be reactive, have a wide range of values, and $\text{NF}(a)$ is not especially reactive toward open-shell species.²

Since $\text{NF}(a^1\Delta)$ possibly could be generated by the $\text{H} + \text{NF}_2$ reaction in practical laser devices, there is a need to know the quenching rate constants by NF_2 and likely precursors to NF_2 , such as NF_3 and N_2F_4 .^{8,9} Although the constants are not well-known, these quenching rates are slow at room temperature and, therefore, the rate constants are difficult to measure in a flow reactor. We have, however, attempted these measurements to establish lower limits to the rate constants. The results obtained here are compared to other measurements in the literature,¹¹⁻¹⁴ usually obtained at higher temperatures. These experiments were done in a glass reactor, and the reactions of the reagents with the walls can generate some SiF_4 . Therefore, the quenching of $\text{NF}(a)$ by SiF_4 also was examined.

The quenching constants and mechanisms for $\text{NF}(a^1\Delta)$ interacting with itself and with $\text{NF}(\text{X}^2\Sigma^-)$ and $\text{NF}(\text{b}^1\Sigma^+)$ are also of practical interest. Since these reactions involve ground-

and/or excited-state potentials of N_2F_2 , they also should be amenable to theoretical treatment. We used the $2\text{F} + \text{HNCO}$ reaction system¹⁵ to generate $\text{NF}(\text{X})$ in a prereactor and then coupled the $\text{NF}(\text{X})$ flow system to the reactor containing $\text{NF}(a)$. The chemical environment is complex, but some reduction in $[\text{NF}(a)]$ was observed for high $[\text{NF}(\text{X})]$, and an estimate of the rate constant for removal of $\text{NF}(a)$ was obtained. Since HNCO and NCO were in the flow reactor for the $\text{NF}(\text{X})$ experiment, we also examined the rates of their reactions with $\text{NF}(a)$. No attempt to study the $\text{NF}(a) + \text{NF}(\text{b})$ reaction was made, and this is a goal for future effort.

The $\text{NF}(a)$ was generated by the $2\text{F} + \text{HN}_3$ reaction using metered flows of $[\text{F}]_0$ and $[\text{HN}_3]_0$ to the prereactor.⁴ Fortunately, there now is a consensus for the rate constants of the primary and secondary steps.^{1,4,16} However, Chen and Dagdigan¹⁷ recently have identified HNF as a product from the $\text{F} + \text{HN}_3$ reaction, which raises a new question about this reaction system. The branching fractions for N_2 and HNF were not established, and we will use $[\text{NF}(a)] = 0.85[\text{HN}_3]_0$ for conditions of excess $[\text{F}]_0$ on the basis of our early study.⁴ If $[\text{F}]_0 > [\text{HN}_3]_0$, the reaction of F with HNF probably gives HNF_2 , which will proceed to $\text{NF}(a) + \text{HF}$ at low pressure, and the branching may not seriously affect the generation of $\text{NF}(a)$. The $\text{NF}(a)$ quenching constants were obtained by adding the reagent of interest to the reactor section of the flow tube and observing the decay of $[\text{NF}(a)]$ by monitoring the $\text{NF}(a-\text{X})$ fluorescence as a function of time for fixed reagent concentration or as a function of reagent concentration for fixed reaction time. It was not possible to search for products from the quenching of $\text{NF}(a)$ in the present study.

Experimental Methods

The apparatus and techniques used to generate $\text{NF}(a)$ and to measure quenching rate constants of $\text{NF}(a)$ by stable molecules have been described in detail.² A 150 cm long and 6.4 cm diameter Pyrex tube, coated with halocarbon wax, served as the flow reactor. The Ar carrier gas was purified by passing the gas through a commercial trap (Matheson 6406) and cooled (196 K) molecular sieve filled traps before being introduced into the reactor. The pressure in the reactor was monitored by a transducer gauge (MKS). A mechanical pump, 1500 L min^{-1} , provided a flow speed of 650 cm s^{-1} at 2–4 Torr. The $\text{NF}(a)$ molecules in the concentration range 10^{11} – $10^{12} \text{ molecule cm}^{-3}$ were produced by the $2\text{F} + \text{HN}_3$ reaction.⁴ The F atoms were generated by passage of a 30% CF_4/Ar mixture together with additional Ar through a microwave discharge. In general, the microwave discharge

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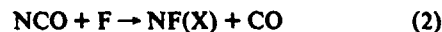
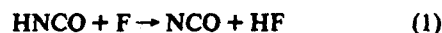
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provides $[F] = 2[CF_4]$, providing that $[CF_4]$ is in the range $0.5\text{--}2 \times 10^{12}$ molecule cm^{-3} ; the dissociation efficiency decreases for higher $[CF_4]$. The F atom and HN_3 flows were introduced at the front of the reactor, and the $F + \text{N}_3$ reaction was complete by the time the flow reached the reagent inlet, which was placed 28 cm (~ 30 ms) downstream from the HN_3 inlet. The front part of the Pyrex tube used for the $2F + \text{HN}_3$ reaction is called the prereactor in the remainder of this paper. Diagrams of the reactor have been given in refs 1 and 2. The deactivation rates of NF(a) by Ar, F, and collisions with the wall have been characterized and all are minor, providing that proper conditioning of the wall has been done and $[F]$ is not too large. Experiments generally were conducted for $[\text{NF(a)}] < 1 \times 10^{12}$ molecule cm^{-3} to minimize the importance of the bimolecular self-destruction rate. However, the $[\text{NF(a)}]$ was 1.2×10^{12} molecule cm^{-3} in the experiments to study the quenching of NF(a) by NF(X), and the bimolecular self-destruction rate ($k_B = (5 \pm 2) \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$) of NF(a) was included in the data analysis of those experiments.

The reagent inlet was attached to the reactor by an O-ring joint, so that changes could be made to accommodate different types of experiments. The reagent concentration in the reactor was obtained from the flow rates and the total pressure. The flow rates for the stable reagent molecules were measured by observing the pressure rise in a 5-L vessel. The reagent flow line was covered by electrical heating tape to permit thermal dissociation of N_2F_4 into NF_2 . The heating tape extended as close as possible to the connection with the main reactor to prevent loss of NF_2 from recombination on the cold surface. The NF_2 flow rate was assigned as 2 times that of the N_2F_4 flow, and the range of $[\text{NF}_2]$ was $0.4\text{--}2.4 \times 10^{15}$ molecule cm^{-3} . The NF_2 recombination rate constant¹⁸ at 300 K is 1.3×10^{-32} $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$, and the loss of $[\text{NF}_2]$ from the homogeneous three-body recombination reaction must be considered for reaction times of 90–120 ms at our Ar pressure. The deactivation rates of NF(a) by SiF_4 and NF_3 are very slow, and high concentrations and long reaction times were needed to see appreciable quenching of $[\text{NF(a)}]$. From a historical perspective, it should be noted that the experimental uncertainty associated with very small rate constants measured in flow reactors frequently is larger than expected.

The NF(X) molecules were generated by reactions of excess F atoms with HNCO in the prereactor. Reactions 1 and 2 have been studied in ref 15; the rate constants at 300 K are 3.4×10^{-11} and 9.2×10^{-12} $\text{cm}^3 \text{s}^{-1}$ for (1) and (2), respectively.



For present purposes it is sufficient to note that $[\text{NF(X)}] = [\text{HNCO}]_0$, if the reaction time and $[F]_0$ are sufficiently large that reaction 2 goes to completion. The bimolecular self-removal rate constant for NF(X) at 300 K is not well-known,¹¹ but it seems to be in the range $(3 \pm 2) \times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$. Thus, self-removal of NF(X) may become important if the concentration becomes larger than $\sim 2 \times 10^{12}$ molecule cm^{-3} . Since the formation rate of NF(X) by reaction 2 is 5 times slower than that of NF(a) from $F + \text{N}_3$,^{1,16} HNCO was introduced into the prereactor using the flow line normally employed for HN_3 , to have as long a reaction time as possible. NF(a) was added to the reactor via a separate miniature prereactor that was attached to the inlet normally used for the quenching reagent. This miniature prereactor was 18 cm long and 2 cm in diameter, and the reaction time was 15–20 ms. To drive the $F + \text{NCO}$ and $F + \text{N}_3$ reactions to completion, excess F concentration was used in both prereactors. The $[\text{NF(a)}]$ and $[\text{NF(X)}]$ values in the main reactor were derived from the $[\text{HN}_3]_0$, $[\text{HNCO}]_0$, and $[F]_0$ values and the reaction rates for reactions 1 and 2 (*vide infra*).

The quenching rates of NF(a) by HNCO and NCO were studied by adding HNCO to the reactor at the reagent inlet, as

in the normal way for stable molecules.¹ The excess F atoms from the prereactor converted some of the HNCO to NCO. Therefore, computer simulation of the concentrations of the reactive mixture along the flow reactor was needed to assign rate constants to NCO and HNCO from the observed total reduction of $[\text{NF(a)}]$.

The HNCO was prepared from the reaction of stearic acid with potassium cyanate under vacuum at 358 K.⁴ The raw product that was collected in a trap at 77 K contained CO_2 , as well as HNCO. The CO_2 was removed by distilling the sample through a trap maintained at 163 K with dynamic pumping. Normally, two distillations were required before the sample was free of CO_2 , as shown by the infrared absorption spectrum. Because a significant fraction of the HNCO polymerizes in the condensed phase, a large part of the HNCO sample was consumed by the purification process. A 1% HNCO/Ar mixture was prepared from the pure sample and stored in a 12-L Pyrex reservoir and metered to the reactor. Freshly prepared HNCO/Ar mixtures were employed for the NF(X) and the HNCO(NCO) quenching experiments so that the $[\text{HNCO}]$ would be reliable.

The SiF_4 , NF_3 , and N_2F_4 tanks were obtained from Matheson, Ozark-Mahoning Inc., and Hercules, respectively. Samples were taken from the tanks and purified by freeze-thaw-pump cycles before being loaded into reservoirs. We found that several freeze-pump-thaw cycles were necessary for purification of the N_2F_4 sample, since it contained N_2 (and perhaps F_2). These three reagents were stored in reservoirs without dilution, since high concentrations were needed to observe quenching of NF(a). The purity of the distilled N_2F_4 sample was confirmed by mass spectrometry.

The detection system was a 0.5-m Minuteman monochromator equipped with a 500-nm blazed grating (1200 grooves mm^{-1}) and a cooled photomultiplier tube (Hamamatsu R-942-02). The monochromator was placed on a table that could be moved along the reactor for observation after a given reaction time.

Experimental Results

Quenching by SiF_4 and NF_3 . Since the bimolecular self-destructive rate is slow for $[\text{NF(a)}] \leq 1 \times 10^{12}$ molecule cm^{-3} , the differential rate law for the decay of NF(a) in the presence of added reagent with concentration $[Q]$ is given by

$$d[\text{NF(a)}]/dt = -(k_Q[Q] + k')[\text{NF(a)}] \quad (3)$$

The quenching rate constant if k_Q and k' is the sum of all other first-order rate constants for removal of NF(a). Providing the glass surface is coated with wax, quenching at the wall is slow and k' is negligible.¹⁻⁴ The integrated rate law has the simple form given by

$$\ln I_a = -(k_Q[Q] + k')t + A \quad (4)$$

where I_a is the intensity of the NF(a-X) emission observed at 850 nm. The radiative lifetime⁶ of NF(a), 5–6 s, is short enough to permit observations of the emission intensity but long enough that radiative decay is not important for reaction times of < 0.4 s. The semilog quenching plots of the NF(a-X) intensity vs added NF_3 and SiF_4 are shown in Figure 1 for the longest feasible reaction times that could be used. High Ar flows were used to maintain a large total pressure and as large a dilution as possible for the NF_3 and SiF_4 reagents. Slopes of the plots are products of the quenching rate constant and the reaction time. The rate constants for NF_3 and SiF_4 with NF(a) are $(1.6 \pm 1.0) \times 10^{-17}$ and $(1.4 \pm 0.5) \times 10^{-16}$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$, respectively, if no corrections are made for back diffusion. Even though the throttling valve was nearly closed to increase the reaction time, the quenching by NF_3 was barely observable for the maximum $[\text{NF}_3]$; note that $[\text{SiF}_4]$ and $[\text{NF}_3]$ approach 0.5 Torr. In fact, the observed change in $[\text{NF(a)}]$ with the addition of NF_3 might be a consequence of effects such as back diffusion and turbulence, rather than quenching. The rate constant reported for NF_3 is

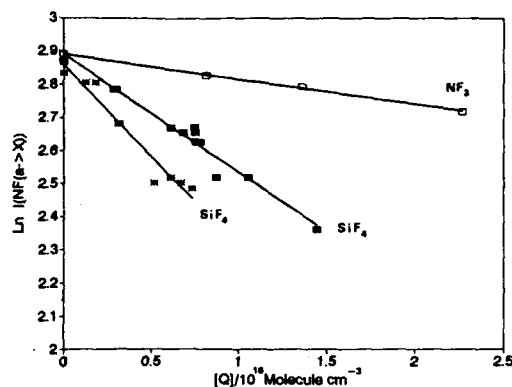


Figure 1. First-order quenching plot of NF(a) by NF₃ and SiF₄. For the NF₃ experiment, [HN₃]₀ and [F]₀ were 1.4×10^{12} and 6.8×10^{12} molecule cm⁻³, respectively, $\Delta t = 0.46$ ms, and the pressure was 8.8 Torr. For the SiF₄ experiments, [HN₃]₀ and [F]₀ were 1.1×10^{12} and 5×10^{12} molecule cm⁻³, respectively, with $\Delta t = 0.31$ ms (□) and 1.2×10^{12} and 5×10^{12} molecule cm⁻³, respectively, with $\Delta t = 0.50$ ms (△); the total pressure was 6.5 Torr.

based upon only one measurement, because we did not want to use large quantities of NF₃, which is rather expensive. This value of k_{NF_3} is 5 times smaller than the one reported previously,⁵ which also should have been reported as an upper limit because very little reduction in [NF(a)] was observed for the range of [NF₃] used in that experiment. We favor the smaller value reported here, which is assigned as an upper limit to the true quenching rate constant at 300 K.

Reduction in [NF(a)] was observed for addition of SiF₄ to the reactor; the two sets of data shown in Figure 1 give $k_{\text{SiF}_4} = (1.4 \pm 0.4) \times 10^{-16}$ cm³ s⁻¹. Although the statistical uncertainty in the measurements was 15%, we assigned a larger absolute uncertainty because of possible turbulence from the addition of the large flow of SiF₄ to the flow reactor.⁴ This value for k_{SiF_4} probably should be considered as an upper limit because of the possible presence of impurities and flow anomalies. The quenching rate by SiF₄ is sufficiently slow that quenching by any SiF₄ present in the NF₂ and N₂F₄ experiments need not be of concern. The SiF₄ reaction rate is very slow, but it seems to be an order of magnitude larger than for NF₃. The quenching rate constants for SF₆ and CF₄ have been reported as $<1 \times 10^{-16}$ and $<0.5 \times 10^{-16}$ cm³ s⁻¹, respectively. These perfluorinated molecules have very small quenching constants for NF(a) because there are no chemical reaction channels, and quenching by an E-V mechanism with repulsive interaction potentials has an extremely slow rate at 300 K.

Quenching by N₂F₄ and NF₂. The reactions of NF(a) with N₂F₄ and NF₂ were studied for various conditions and reaction times. Daily degassing of the N₂F₄ sample was necessary because of thermal decomposition. The quenching data for N₂F₄ with several different [NF(a)] values and reaction times are shown in Figure 2. The rate constants obtained from the longer reaction times (see plots b and e of Figure 2) are in a good agreement with those obtained from the shorter reaction times. The average rate constant for quenching of NF(a) by N₂F₄ was $(4.0 \pm 1.0) \times 10^{-15}$ cm³ s⁻¹ from the data in Figure 2. Similar rate constants were obtained for the different conditions, and the N₂F₄ rate constant was reproducible, at least for this sample of N₂F₄. The rate constant is approximately 200 times larger than k_{NF_3} .

The NF₂ was introduced into the flow reactor by heating the N₂F₄ flow line to 500 K. For these conditions more than 98% of the N₂F₄ is converted to NF₂, according to thermal equilibrium data. We assumed that the N₂F₄ flow was fully dissociated upon entry to the flow reactor. When a given N₂F₄ flow was heated, a reduction in the degree of quenching of NF(a) always was observed. Thus, k_{NF_2} must be smaller than $k_{\text{N}_2\text{F}_4}$. However, identification of the proper [NF₂] value for the relatively long reaction times must be done carefully to obtain a value for k_{NF_2} .

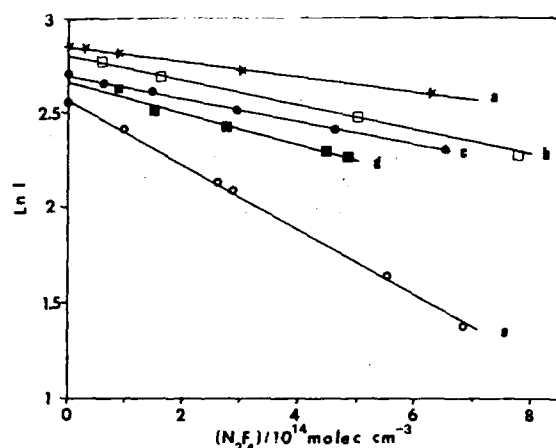


Figure 2. First-order quenching plots of NF(a) from five independent N₂F₄ experiments with [F]₀ = 3[HN₃]₀ and a total pressure of 3.2 Torr. (a) [NF(a)] = 1.5×10^{12} molecule cm⁻³ and $\Delta t = 84$ ms; (b) [NF(a)] = 4.4×10^{11} molecule cm⁻³ and $\Delta t = 210$ ms; (c) [NF(a)] = 1.5×10^{12} molecule cm⁻³ and $\Delta t = 150$ ms; (d) [NF(a)] = 1.2×10^{12} molecule cm⁻³ and $\Delta t = 150$ ms; (e) [NF(a)] = 9.8×10^{11} molecule cm⁻³ and $\Delta t = 380$ ms.

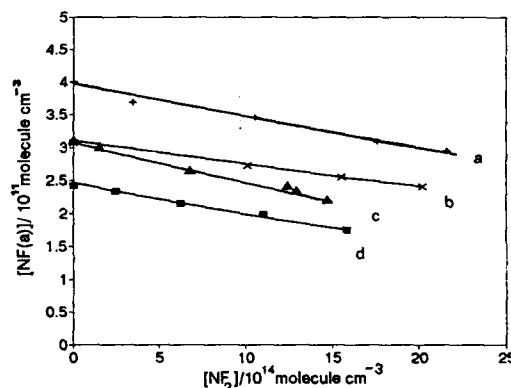


Figure 3. Plots of the reduction in [NF(a)] vs the ideal NF₂ concentration; [NF₂]₀ = 2[N₂F₄]. The continuous curves are the computer simulation for the following reaction times, [NF₂]₀, and Ar pressure: (a, +) Ar = 3.1 Torr, $\Delta t = 89$ ns, [NF(a)]₀ = 4.2×10^{11} molecule cm⁻³; (b, ×) Ar = 3.1 Torr, $\Delta t = 148$ ms, [NF(a)]₀ = 2.8×10^{11} molecule cm⁻³; (c, △) Ar = 3.1 Torr, $\Delta t = 148$ ms, [NF(a)]₀ = 4.2×10^{11} molecule cm⁻³; (d, ■) Ar = 3.1 Torr, $\Delta t = 83$ ms, [NF(a)]₀ = 2.8×10^{11} molecule cm⁻³. The k_{NF_2} and $k_{\text{N}_2\text{F}_4}$ values used to fit plots were 1.6×10^{-15} and 4.0×10^{-15} cm³ molecule⁻¹ s⁻¹.

from the observed decay of the [NF(a)]. Since the rate constant¹⁸ for three-body recombination of NF₂ in Ar is 1.3×10^{-32} cm⁶ molecule⁻² s⁻¹, a significant fraction of the [NF₂] recombines to N₂F₄ for reaction times of 80–120 ms in 2.3 Torr of Ar. Thus, a standard first-order plot of ln[NF(a)] vs [NF₂] for fixed reaction time is not a valid way to obtain the rate constant. The following reactions must be considered in evaluating the data shown in Figure 3.



The differential rate laws describing the NF(a), NF₂, and N₂F₄ concentrations were numerically integrated, and the calculated results for the decay of [NF(a)] were fitted to the data of Figure 3 to obtain k_{NF_2} . A N₂F₄ quenching rate constant of 4×10^{-15} cm³ s⁻¹ and an Ar pressure of 2.3 Torr were used for the simulation. The initial concentrations of NF(a) and NF₂ were obtained from

TABLE I: Quenching Rate Constant of NF(a¹Δ) at Room Temperature^{a,b}

reagent	this work (10 ⁻¹⁴ cm ³ molecule ⁻¹ s ⁻¹)	other studies (10 ⁻¹⁴ cm ³ molecule ⁻¹ s ⁻¹)
NF(X)	30 ± 10	
NF ₂	0.16 ± 0.04	0.09; ^c 0.027 ± 0.010 ^d
N ₂ F ₄	0.40 ± 0.10	0.012 ± 0.001 ^c
NF ₃	≤ 0.0016 ± 0.0010	0.0074 ± 0.0007 ^c
SiF ₄	≤ 0.014 ± 0.005	
HNCO	70 ± 20	
NCO	45 ± 15	

^a The self-quenching constant of NF(a) is $(5 \pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. ^b The quenching rate constant by F atoms is $(4 \pm 2) \times 10^{-13}$ cm³ s⁻¹; this rate constant was used for the kinetic models used to obtain $k_{\text{NF(X)}}$, k_{NCO} , and k_{HNCO} . ^c Reference 11; k_{NF} was measured at 423 K; $k_{\text{N}_2\text{F}_4}$ was measured at 297 K. ^d Reference 12; k_{NF} was measured at 443 K, and this result has been confirmed by work in ref 11. ^e Reference 14, calculated from the recommended Arrhenius parameters.

the measured flows of HN₃ and N₂F₄; [NF₂]₀ was set as 2[N₂F₄]. Four sets of independent experimental results are shown in Figure 3 and compared with the calculated decay of [NF(a)]. A quenching rate constant by NF₂ of 1.6×10^{-15} cm³ s⁻¹ gave the best overall fit. Because of the uncertainty in [NF₂] and other possible complications in the complex chemical environment, the uncertainty of the rate constant was estimated as ±30%. Therefore, k_{NF_2} is listed as $(1.6 \pm 0.4) \times 10^{-15}$ cm³ s⁻¹ in Table I. After passing the N₂F₄ through the heated inlet at these high concentrations, we did observe some white powder in the glass tube, so [NF₂]₀ could be somewhat less than 2[N₂F₄]. However, less quenching of NF(a) was always observed when a given N₂F₄ flow was heated; i.e., dissociating the N₂F₄ to 2NF₂ gave a higher [NF(a)], and therefore, it seems to be clearly established that $k_{\text{NF}_2} < k_{\text{N}_2\text{F}_4}$.

Quenching by HNCO, NCO(X), and NF(X). Since the flow rate of HNCO determines the concentration of NF(X), the purity of HNCO is an important aspect of these experiments. The HNCO sample was freshly prepared and purified as described under Experimental Methods. For the NF(X) quenching experiment, the HNCO was introduced into the main prereactor, and HN₃ was added to a second small prereactor attached to the inlet normally used for the reagent. The [F]₀ in both prereactors was 1×10^{13} atom cm⁻³. The NF(X) formed in the prereactor (the reaction time for the 2F + HNCO reaction was 40 ms) was mixed with the NF(a) flow at the reagent inlet. A relatively large NF(a) concentration was selected, 1.2×10^{12} molecule cm⁻³, to have a strong NF(a-X) signal. The [NF(a)] was determined by comparing the NF(a-X) intensity from this experiment with the intensity from a known concentration of NF(a) formed in the usual way for [F]₀ > 2[HN₃]₀ in the main reactor. The [HNCO]₀ was 3×10^{12} and 6×10^{12} molecule cm⁻³ for the two experiments, giving [NF(X)] at the NF(a) inlet of 2.6×10^{12} and 4.8×10^{12} molecule cm⁻³, based on numerical integration of the rate equations for reactions 1 and 2. Since the NF(a) flow also contained excess [F], the residual NCO was converted to NF(X) a few centimeters beyond the mixing point. Consequently, the data in Figure 4 are for the interaction of NF(a) with NF(X). Although the CO concentration will be equal to the NF(X) concentration, the CO rate constant for quenching NF(a) is only 3.6×10^{-15} cm³ s⁻¹ and removal of NF(a) by CO is not important. The quenching of NF(a) by NF(X) was not measured by the fixed point method; rather, the decay of [NF(a)] was recorded along the reactor with and without a given [NF(X)]. Figure 4A,B shows the two experimental sets of data with and without the added NF(X); the experiment with the smaller [NF(X)] hardly shows any removal of NF(a). The most important result is the qualitative conclusion that NF(a) is not rapidly removed by NF(X) concentrations of $3\text{--}6 \times 10^{12}$ molecule cm⁻³; thus, $k_{\text{NF(X)}}$ must be smaller than the NF(a) bimolecular self-quenching rate constant, $(5 \pm 2) \times 10^{-12}$ cm³ s⁻¹. The kinetic model below, including self-quenching of NF(a),

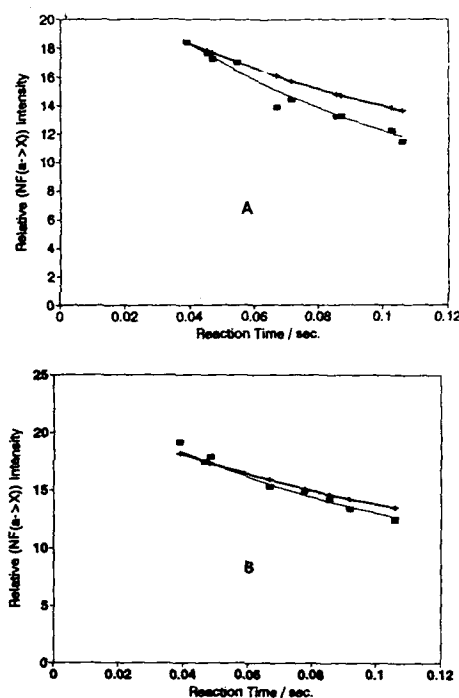
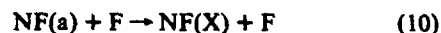
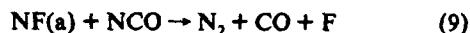
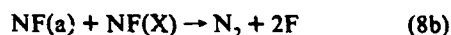
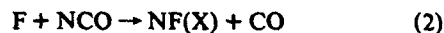


Figure 4. Comparisons of experimental and calculated results for the quenching of NF(a) by NF(X). Each experiment shows the relative [NF(a)] vs time in the absence (+) and presence (■) of NF(X); the total pressure was 3.2 Torr. In the small prereactor [HN₃]₀ = 1.8×10^{12} and [F]₀ = 1×10^{13} cm⁻³, giving [NF(a)] = 1×10^{12} molecule cm⁻³. The solid lines are the simulated results; see text for the kinetic model and the rate constants. (A) In the main reactor [HNCO]₀ = 6×10^{12} and [F]₀ = 1×10^{13} cm⁻³, which gave [NF(X)]₀ = 4.8×10^{12} and [NCO] = 1.2×10^{12} molecule cm⁻³ at the NF(a) inlet. (B) In the main reactor [HNCO]₀ = 3×10^{12} and [F]₀ = 1×10^{13} cm⁻³, which gave [NF(X)] = 2.6×10^{12} and [NCO] = 4×10^{11} molecule cm⁻³ at the NF(a) inlet.

was used to assign a quenching rate constant to NF(X) from the data in Figure 4.



The bimolecular self-destruction reaction of NF(X) was not included because the rate constant is not well-known.¹¹ If a significant amount of NF(X) was removed, then the rate constant derived for reactions 8a and 8b will be a lower limit to the true value. In the first analysis we assumed physical quenching for the deactivation of NF(a) by NF(X), so [NF(X)] was augmented by reaction 8a. Another possibility would be reaction 8b, which would reduce [NF(X)]. The differential rate law for the decay of NF(a) was expressed by

$$-d[\text{NF(a)}]/dt = k_s[\text{NF(a)}]^2 + (k_F[\text{F}] + k_{\text{NF(X)}}[\text{NF(X)}] + k_{\text{NCO}}[\text{NCO}])[\text{NF(a)}] \quad (11)$$

Although the F atom concentration was relatively high, the degree of quenching by F atoms actually was minor. The NCO reaction also was included (with the rate constant assigned from independent experiments in the next section), although the NF(X) concentration was always much higher than the NCO concentration. Fitting the data in Figure 4 gave a rate constant of (3.5

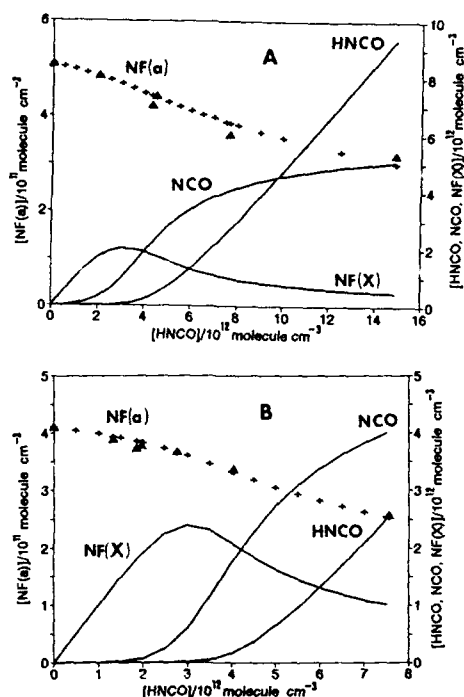


Figure 5. Plot of the decay of $[NF(a)]$ vs added $[HNCO]_0$ for reaction times of 0.076 (A) and 0.143 s (B). The calculated results for the values of k_{NCO} and k_{HNCO} given in Table I are shown by the + points. The solid curves show the calculated $NF(X)$, NCO , and $HNCO$ concentrations at the observation point.

$\pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for reaction 8a. In the second set of calculations, reaction 8b was assumed to be the quenching mechanism and the best fit was with $(2.5 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. This mechanism gives a somewhat smaller rate constant because $[NF(X)]$ is not enhanced and because F atoms are generated. We cannot distinguish between reactions 8a and 8b; therefore, a rate constant of $(3 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ was chosen. The calculated results shown in Figure 4 are for this rate constant. The rate constant for quenching of $NF(a)$ by $NF(X)$ seems to be an order of magnitude smaller than the self-quenching constant of $NF(a)$.

The quenching of $NF(a)$ by $HNCO$ and NCO was studied by the fixed point method. The $NF(a)$ molecules were generated in the main prereactor in the usual way, and $HNCO$ was introduced into the main reactor from the reagent inlet. Because a large amount of the 1% $HNCO/\text{Ar}$ mixture was needed to obtain observable quenching, only a few experiments with the $HNCO/NCO$ system were conducted. The decay of $NF(a)$ was measured for reaction times of 76 and 143 ms, and the experimental results are shown in Figure 5. Because of the presence of F atoms from the prereactor, some of the $HNCO$ was converted to NCO and even to $NF(X)$ for low $[HNCO]$. Therefore, the reduction in $[NF(a)]$ shown in Figure 5 was related to the rate constants for $HNCO$ and NCO by computer simulation of a model that included reactions 1, 2, 8, and 9 and quenching by $HNCO$. The chemical composition in the reaction after 0.076 and 0.14 s is shown in Figure 5. For the higher flow rates of $HNCO$, most of the quenching is by NCO and $HNCO$.

Calculations were done first for the longer reaction time (lower $HNCO$ flows), since $[NCO]$ was the dominant species removing $NF(a)$. Then the shorter time experiment was fitted to obtain a better measure of the role of $HNCO$. After numerous trials, the final selections were $k_{NCO} = (7.0 \pm 2.0) \times 10^{-13}$ and $k_{HNCO} = (4.5 \pm 1.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. The present experimental design was appropriate for the measurement of k_{NCO} . A better experimental design for measuring k_{HNCO} would have been to use reduced $[F]_0$ with larger $[HNCO]$. However, the required amount of $HNCO$ was not available at the time the experiment

could be done. The values assigned to k_{NCO} and k_{HNCO} depend upon the rate constants for reactions 1 and 2 and to some extent on $k_{NF(X)}$, and it is difficult to evaluate their absolute reliability. The fitting to the data actually was rather sensitive to the values for the rate constants, and that is the origin of the $\pm 30\%$ estimate of the uncertainty. This estimate does not include the uncertainty in the rate constants for reactions 1 and 2 and the uncertainty in $[F]_0$. The absolute uncertainty is probably $\pm 50\%$.

Discussion

The room temperature rate constants obtained in this work are summarized in Table I and compared to other measurements. Before the N_2F_4 series of reagents is considered, the results for $HNCO$, NCO , and SiF_4 will be discussed. The rate constant for $HNCO$ is about 2 times larger than that for HN_3 .¹ The $HNCO$ molecule and $NCO(X^2\Pi)$ radical are carbonyl compounds, and their rate constants can be compared to those for CO , OCS , and $(CH_3)_2CO$, which are 0.36×10^{-14} , 6.0×10^{-14} , and $3.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, respectively.¹ The reaction with CO is known to proceed by addition over a small activation energy barrier, giving $FNCO$ that subsequently dissociates to $F + NCO$ at low pressure.⁷ The k_{NCO} and k_{HNCO} values are similar to that of acetone, and the interaction of $NF(a)$ with $HNCO$ and NCO probably proceeds by interaction with a lone pair of electrons on the oxygen atom or with the $C=O$ double bond. The slow rates of reaction for SiF_4 and NF_3 are consistent with results for other perfluorinated molecules, such as CF_4 and SF_6 , which have rate constants that are too small to measure at 300 K in the flow reactor. These rates are slow because there are no attractive interaction potentials to connect the $NF(a^1\Delta)$ entrance and $NF(X^3\Sigma^-)$ exit channels for an E-V quenching mechanism.

Weiller and co-workers¹¹ have used the photolysis^{8,10} of NF_2 as a source of $NF(a)$ and $NF(X)$ to measure some rate constants using real time monitoring of $[NF(a)]$ and $[NF(X)]$. Most experiments were done at ~ 420 K to obtain an adequate NF_2 concentration from thermal dissociation of N_2F_4 . They did experiments with O_2 and I_2 to calibrate their experimental method vs the flow reactor technique. Extrapolation of the Du and Setser rate constant data³ for O_2 to 421 K gave good agreement with the rate constant measured according to the static photolysis method. Thus, the photolytic method generally should be reliable, providing there are no chemical complications from the added reagent.

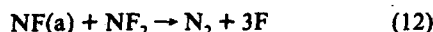
Weiller et al. measured the quenching rate constant for NF_3 as $(7.4 \pm 0.7) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 423 K. Given the large uncertainty in our 300 K value of $(1.6 \pm 1.0) \times 10^{-17}$, these two measurements should be considered to be in agreement. The quenching rate constant for NF_3 certainly is small, and the lone pair on NF_3 is not sufficiently basic to enable adduct formation with $NF(a)$. In contrast, the quenching constant for NH_3 is $3.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$; the quenching constants for amines generally increase as the base strength of the molecule increases.⁷

The agreement between the quenching rate constants for N_2F_4 measured according to the flow reactor and static photolytic methods is less pleasing. Both measurements are at room temperature, but our rate constant is 30 times larger than the value obtained by Weiller et al.¹¹ They considered the possibility that the quenching was from NF_2 in equilibrium with N_2F_4 , but that explanation would make their $k_{N_2F_4}$ even smaller. The difference between the measurements may partly be a consequence of the purities of the N_2F_4 samples from the two laboratories. After the experiments were completed, we checked the purity of a N_2F_4 sample from our tank prior to distillation. We found that N_2 comprised about 30% of the gas. A mass spectrum of a distilled sample showed only NF_2^+ and $N_2F_4^+$; there was no peak corresponding to HF^+ . As already mentioned, we removed the F_2 and N_2 from our sample (originally obtained from Hercules) by distillation prior to each experiment. The $NF(a)$ quenching rate constants for the likely impurities, such as HF , F_2 , and N_2 ,

are small, 3×10^{-15} , 3.2×10^{-14} , and $<1.2 \times 10^{-17}$ cm³ s⁻¹, respectively. Decomposition of the N₂F₄ sample to N₂ (and F₂ which probably reacts with the walls) in the Aerospace Laboratory could explain part of the difference, but that is unlikely to be the total explanation. Another possibility is the different chemical environments for the two experiments, which is mainly the presence of excess F atoms in our flow reactor. But partial formation of NF₃ and NF₂ from F + N₂F₄ cannot explain the difference, since k_{NF_3} and k_{NF_2} are both smaller than $k_{\text{N}_2\text{F}_4}$. The explanation for the difference in the $k_{\text{N}_2\text{F}_4}$ values and unambiguous identification of the correct value remain goals for future experiments.

The difference between the measurements from the two laboratories carries over to the rate constants for NF₂, which lends some support to the idea that the quality of the N₂F₄ samples is the source of the discrepancy. Our value for k_{NF_2} at 300 K is 5 times larger than the Aerospace value at 443 K. We concluded that k_{NF_2} is ~3 times smaller than $k_{\text{N}_2\text{F}_4}$ at 300 K. Since both measurements were done in the same apparatus at the same time, the claim that $k_{\text{NF}_2} < k_{\text{N}_2\text{F}_4}$ should be reliable. The rate constants from the Aerospace Laboratory for NF₂ and N₂F₄ were not measured at the same temperature, but if $k_{\text{N}_2\text{F}_4}$ increases with temperature, their ratio of rate constants could be similar to ours.

A Russian group^{13,14} has studied chain branching in the NF₂ + H₂ reaction. They included reaction 12 as the chain-branching



step and obtained an Arrhenius expression of $(2.75 \pm 1.15) \times 10^{-15} \exp(-3095 \pm 335/T)$ cm³ s⁻¹ from the self-ignition limits. The Arrhenius expression gives 9.1×10^{-16} cm³ s⁻¹ at 300 K, which compares favorably with an independent room temperature measurement ($k_{\text{NF}_2} = 6.7 \times 10^{-16}$ cm³ s⁻¹) from the same Russian group. Considering the complexity of the analysis, their rate constant is surprisingly close to our 300 K value of 16×10^{-16} cm³ s⁻¹. The 443 K rate constant from the Russian group is 90 times larger than the Aerospace value. Some reservations probably should be maintained because the Russian group claimed that NF(X) does not react with NF₂. They did not include this reaction in their kinetic model, whereas Weiller et al. have shown that this rate constant is $(2.4 \pm 0.2) \times 10^{-12}$ cm³ s⁻¹ at 420 K by directly monitoring the decay of [NF(X)] in NF₂. The NF(X) + NF₂ reaction should proceed via the ground-state potential of N₂F₃, whereas the NF(a) + NF₂ reaction would probably involve an excited-state N₂F₃ potential. Isolation of the elementary reaction between NF(a) and NF₂ with measurement of the rate constant as a function of temperature and identification of the products is clearly an item of high priority for future utilization of the H + NF₂ reaction for obtaining NF(a). The release of F atoms to the reaction system by eq 12 can have serious implications.

There are no other measurements, to our knowledge, for the interaction between NF(a¹Δ) and NF(X³Σ⁻). Although the degree of observed quenching was not large, the magnitude of the rate constant, $k_{\text{NF(X)}} = (3 \pm 1) \times 10^{-13}$ cm³ s⁻¹, should be reliable. We did not allow for bimolecular removal of NF(X). If that rate is found in the future to be significant, then the above value for $k_{\text{NF(X)}}$ must be increased. The *ab initio* calculations for N₂F₂ by Brener¹⁹ are only for the ground state, which would correlate to 2NF(X). The NF(X) + NF(a) reaction could proceed by an excited triplet potential of N₂F₂ that dissociates to N₂ + 2F. Alternatively, the entrance channel triplet potential correlating to NF(X) + NF(a) could interact with an exit channel triplet potential correlating to 2NF(X), and the products could be 2NF(X³Σ⁻). The relatively small rate constant (for interaction

of two radicals) is consistent with the slow rates of interaction of NF(a) with many open-shell atoms and radicals.² The reaction rate is slower than the self-destruction reaction ($k_9 = (5 \pm 2) \times 10^{-12}$ cm³ s⁻¹) of NF(a), which probably proceeds by an excited singlet state of N₂F₂. Weiller and co-workers¹¹ have reported a rate constant of $(3.5 \pm 2) \times 10^{-12}$ cm³ s⁻¹ for the self-destruction rate constant of NF(X) at 420 K. For future utilization of high concentrations of NF(a), more accurate values of the rate constants with temperature coefficients for reactions 8a and 8b and the self-destruction reaction are needed. *Ab initio* calculations of the excited-state potentials of N₂F₂ would be very helpful in interpreting the bimolecular reactions among the NF(X), NF(a), and NF(b) pairs.

Conclusions

Our work at 300 K, together with other measurements¹¹ at higher temperatures, shows that the quenching rate of NF(a) by NF₃ is very slow. The rate constant is smaller, but comparable, to other perfluorinated molecules such as SiF₄, CF₄, and SF₆. The rate constants for NF₂ ($(1.6 \pm 0.4) \times 10^{-15}$ cm³ s⁻¹) and NF(X) ($(3.0 \pm 1.0) \times 10^{-13}$ cm³ s⁻¹) are considerably larger. The rate constant for N₂F₄ is 2–3 times larger than that for NF₂. However, there is a lack of agreement between our work and that of other laboratories¹¹ for the value of the N₂F₄ rate constant, and experiments are needed with other techniques to resolve the difference. The products from quenching of NF(a) by NF(X), NF₂, and N₂F₄ were not measured. The 2F + HNCO reaction system was used to generate known concentrations of NF(X) in the flow reactor.

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